Origin of Band Modulation in GeTe-rich Ge-Sb-Te Thin Film

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	From EPMA (WDS)			From ICP-OES			From XPS		
	Ge	Sb	Te	Ge	Sb	Te	Ge	Sb	Te
Before ^{a)}	0.594	0.106	1						
Annealed ^{b)}	0.597	0.106	1	0.632	0.102	1	0.566	0.171	1
Heated ^{c)}	0.581	0.106	1						

 Table 1. Atomic composition of Ge-Sb-Te thin film using different analysis method

^{a)}This sample was obtained right after RF deposition (sample is still amorphous)

^{b)}This sample was obtained after deposition and after post-annealing treatment (sample used prior to TE measurements)

^{c)}This sample was obtained after being heated (similar to heating profile during TE measurements) – sample should be in this state after various temperature dependent studies



Figure S1. Composition of our GST film compared with target composition and known pseudo-binary tie line of GeTe and Sb₂Te₃.



Figure S2. Temperature-dependent X-ray diffraction pattern. The index refers to the rock-salt cubic structure of Ge-Sb-Te as reported by ICSD#165413.



Figure S3. Comparison of temperature-dependent thermoelectric parameters from our own measurement (filled circle) and from our collaborator's (open circle) measured using ULVAC ZEM-3 measurement system.



Figure S4. Observation of a similar trend from a different sample (Ge_{0.61}Sb_{0.12}Te). Temperature-dependent a, electrical conductivity, b, Seebeck coefficient and c, power factor



Figure S5. Thermoelectric parameters of the Si substrate a, Seebeck coefficient and b, electrical resistivity.



Figure S6. Temperature-dependent Hall coefficient.



Figure S7. Temperature-dependent carrier concentration from Hall measurements from various samples



Figure S8. Band structure of the GeTe crystal containing both a Ge vacancy and an Sb atom substituting a near-neighbor Ge atom in a 4 x 4 x 4 supercell. The energy bands are

back folded to the first Brillouin zone of the perfect GeTe crystal using the methods in Refs. 50 and 51.



Figure S9. Full-scale temperature-dependent ultraviolet photoemission spectra showing the valence band spectra and work function. The intersection point of fitted lines labeled "x" and "y" indicating the valence band edge while the intersection point of fitted lines labeled "a" and "b" indicating the work function.



Figure S10. Temperature-dependent x-ray photoemission spectra. Spectral region is limited to the Ge 3d, Sb 4d and Te 4d lines of the sample.



Figure S11. Typical fitting of X-ray photoemission spectra. **a**, and **c**, are spectra obtained at room temperature while **b**, and **d**, are spectra obtained at 200 °C. Spectra of Sb 3d and Te 3d were used for further analysis in the main text to minimize effects of overlapping peaks during fitting.



Figure S12. Temperature-dependent TEM images and corresponding SAED pattern indicating the changes in the lattice constant observed.



Figure S13. Comparison of lattice constants. Lattice constants obtained from various reported coefficient of thermal expansion (CTE) of related materials (GeTe⁵⁶; Ge₂Sb₂Te⁵⁷) and substrates (Si⁵⁸). Notably, the lattice constant changes in our film as measured from the temperature-dependent XRD showed a more significant increase with temperature.



Figure S14. Comparison of lattice constants of various known Fm-3m space group compounds from different orientations.



Figure S15. Lattice constants of GST film from different orientations at five thermal cycles. (LT represents lattice constants at 30°C and HT represents lattice constants at 300°C, while the bottom number indicates the thermal cycle number).



Figure S16. Temperature-dependent TEM micrographs of GST film with the green arrow as marker of location and the red circle region indicating the presence of stacking faults after transition temperature. Scale bar is 20 nm.



Figure S17. SEM images of the post-annealed film. **a**, plan view and **b**, cross-section view.

Reference and Notes

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